# Variational Monte Carlo for spin-orbit interacting systems

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Recently, a diffusion Monte Carlo algorithm was applied to the study of spin-dependent interactions in condensed matter [A. Ambrosetti, F. Pederiva, E. Lipparini, and S. Gandolfi, Phys. Rev. B **80**, 125306 (2009)]. Following some of the ideas presented therein, and applied to a Hamiltonian containing a Rashba-like interaction, a general variational Monte Carlo approach is here introduced that treats in an efficient and very accurate way the spin degrees of freedom in atoms when spin-orbit effects are included in the Hamiltonian describing the electronic structure. We illustrate the algorithm on the evaluation of the spin-orbit splittings of isolated C, Tl, Pb, Bi, and Po atoms. In the case of the carbon atom, we investigate the differences between the inclusion of the spin orbit in its realistic and effective spherically symmetrized forms. The method exhibits a very good accuracy in describing the small energy splittings, opening the way for systematic quantum Monte Carlo studies of spin-orbit effects in atomic systems.

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## I. INTRODUCTION

In the last few decades, quantum Monte Carlo (QMC) techniques were successfully applied to a large number of systems in different fields of physics, quantum chemistry, and materials science.[1–3] The high accuracy obtained and the possibility of treating a relatively large number of particles within an affordable computational cost have certainly been the key ingredients for such a success. A fundamental property of QMC methods resides also in their scalability, which, due to the introduction and recent proliferation of massively parallel systems, makes a good case for a future applicability to large quantum many-body systems, up to now mainly investigated by means of density functional methods. Several years ago, an extension of the diffusion Monte Carlo (DMC) algorithm, employing an efficient recasting of Green's function, was applied to many nucleon systems with interactions depending on the spin and isospin degrees of freedom.[4] This seminal paper has opened the way to studies of broad classes of systems in which spin related effects play a fundamental role. Most successful applications so far pertain to the field of nuclear physics.[5] However, in the last few years the method was extended to many electron systems, and in particular to the study of the two-dimensional homogeneous electron gas[6,7] and parabolic quantum dots.[8] These models are often used to describe quasi-two-dimensional nanostructures built on semiconductor heterojunctions, where the confining potential shows an asymmetry giving rise to a transverse electric field interacting with the moving electrons. This coupling can be described by an effective Rashba spin-orbit Hamiltonian. The next natural extension of the method in condensed matter applications is the study of spin-orbit (SO) effects in atoms, molecules, and solids. Preliminary estimations show that QMC methods should be able to provide the necessary accuracy

and affordability for bringing to a completely new level the theoretical investigation in this area. The extension is highly nontrivial, mostly due to the technical issues that might in principle limit the accuracy of a QMC calculation in presence of a noncentral interaction.

One of the main issues concerning the DMC method is the need for trial wave functions, i.e., accurate approximations to the exact solution of the Schroedinger's equation. The availability of a good trial wave function represents a crucial challenge both at the computational and at a more fundamental level. The trial wave function not only affects the computational efficiency of the DMC calculation, but for Fermionic systems, determines the accuracy of the final result as a consequence of the necessity of applying the so-called "fixed-node" approximation.[9–11] An additional problem which comes to the forefront in the case of spin-orbit interaction is the necessity to deal with operators which do not necessarily commute with the rest of the Hamiltonian.

Both these problems are usually tackled via a preliminary variational Monte Carlo (VMC) approach. Regarding the first challenge, VMC is an important, effective way of dealing with optimization of trial wave functions including almost arbitrarily complex many-body correlations.[12,13] Concerning the second issue, the DMC expectations of operators (denoted as $O$) not commuting with the Hamiltonian is known to be biased by errors depending on the trial wave function accuracy as well, so that efficient optimization is again an important way to alleviate this problem. In DMC, such errors stem from the way DMC expectation values are computed:

$$\langle O \rangle_{DMC} = \frac{\langle \phi_T | O | \psi \rangle}{\langle \phi_T | \psi \rangle}. \quad (1)$$

Here $\phi_T$ represents the trial wave function while $\psi$ is the DMC ground state of the system. If $[O,H] = 0$ this in principle

introduces no bias since $\psi$ is an eigenstate of $H$. If this is not the case, the estimate is affected by a bias depending on $\phi_T$, and it is usually corrected to the leading order by using the formula

$$\langle\psi|O|\psi\rangle \sim 2\langle\phi_T|O|\psi\rangle - \langle\phi_T|O|\phi_T\rangle, \qquad (2)$$

where integrals are normalized, and the last term corresponds to the VMC estimate of the operator $O$ over $\phi_T$.

From these arguments it is possible to grasp how an efficient VMC algorithm capable of explicitly dealing with spin degrees of freedom is of significant importance, not only as a robust and reliable numerical method itself, but also for the development of the more sophisticated QMC algorithms.

In this paper we present the theory, the Monte Carlo algorithm, and the results assessing the possibility of developing wave functions containing the necessary correlation at the *antisymmetric* level (i.e., in the part of the wave function which is usually described by a Slater determinant) by means of a variational procedure. The many-body correlations that are usually introduced in order to describe the short range effects of the Coulomb interaction are neglected on purpose for the C atom in order to make the peculiar aspects of the spin-dependent algorithm clear. Two-body correlations are instead introduced in calculations relative to the more relevant cases of heavier atoms. The paper is organized as follows. In Section II the VMC algorithm and the structure of the spinorial wave functions used in the calculations are illustrated. Section III presents applications to the evaluation of spin-orbit splittings in C, Tl, Pb, Bi, and Po. Section IV is devoted to conclusions.

## II. METHOD

Variational Monte Carlo is a very efficient algorithm for evaluating expectation values of observables over a given trial wave function through the computation of integrals of the kind

$$\frac{\langle\psi_T|O|\psi_T\rangle}{\langle\psi_T|\psi_T\rangle}. \qquad (3)$$

Its efficiency is basically due to a stochastic integration which yields statistical errors for the integral estimate decreasing as $N_{\text{iter}}^{-1/2}$ ($N_{\text{iter}}$ stands for the number of iterations), irrespective of the integral dimensionality.

When one is restricted to Hamiltonians or operators with no explicit spin dependence, it is not necessary to perform the summations over the spin degrees of freedom. These become static variables, and can simply be treated as labels. As a consequence, once a spin state and spin labels have been specified, the equation above can be rewritten as

$$\frac{\int dR \psi_T^*(R)\psi_T(R)\frac{O\psi_T(R)}{\psi_T(R)}}{\int dR \psi_T^*(R)\psi_T(R)}, \qquad (4)$$

where $R$ here represents the space coordinates for the system.

On the other hand, for Hamiltonians containing spin-orbit interactions, the same simplification is not correct. The trial wave function will be, in general, made up with Slater determinants containing single particle spinors, and all the spin variables should be in this case taken into account explicitly. Spinors in general have nontrivial forms, and the spin state of

the single particles could change as a function of the space coordinates. This means that in general one needs to perform a summation over a complete spin basis:

$$\int dR \sum_S \frac{\langle\psi_T|R,S\rangle\langle R,S|O|\psi_T\rangle}{\langle\psi_T|\psi_T\rangle}. \qquad (5)$$

Clearly, one way or another, one has to sample the relevant degrees of freedom in order to evaluate the impact of the spin on the expectation values. One possible way is to sum over the spin variables, i.e., sample the $2^N$ discrete space.

What is proposed here is an alternative approach in which integration over auxiliary variables takes the place of the discrete sum. Although the number of integration variables is increased, exploiting the VMC algorithm this can be performed without significant loss of computational efficiency.

The trial wave function which we employ in calculations is a single Slater determinant of single-particle spinors. Let us first consider the simple two-electron case in order to illustrate the method. The spinors we will use are

$$\vec{\psi}_1 = \begin{pmatrix} \psi_1^1 \\ \psi_2^1 \end{pmatrix} \quad \vec{\psi}_2 = \begin{pmatrix} \psi_1^2 \\ \psi_2^2 \end{pmatrix}. \qquad (6)$$

The spacial coordinates of the two electrons will be $\vec{r}_1$ and $\vec{r}_2$, while the spin coordinates can be parametrized as follows:

$$\vec{s}_1 = \begin{pmatrix} \sin(\alpha_1)e^{i\delta_1} \\ \cos(\alpha_1) \end{pmatrix} \quad \vec{s}_2 = \begin{pmatrix} \sin(\alpha_2)e^{i\delta_2} \\ \cos(\alpha_2) \end{pmatrix}. \qquad (7)$$

The Slater determinant can be written as

$$\Phi(\vec{r}_1,\vec{s}_1,\vec{r}_2,\vec{s}_2) = \det\begin{pmatrix} \langle\vec{s}_1,\vec{r}_1|\vec{\psi}_1\rangle & \langle\vec{s}_1,\vec{r}_1|\vec{\psi}_2\rangle \\ \langle\vec{s}_2,\vec{r}_2|\vec{\psi}_1\rangle & \langle\vec{s}_2,\vec{r}_2|\vec{\psi}_2\rangle \end{pmatrix}. \qquad (8)$$

A complete spin basis for this system is $\uparrow\uparrow,\uparrow\downarrow,\downarrow\uparrow,\downarrow\downarrow$, so that, given a second wave function $\Phi'$ of the same form as $\Phi$, the following equality holds:

$$\langle\Phi|\Phi'\rangle = \langle\Phi|\uparrow\uparrow\rangle\langle\uparrow\uparrow|\Phi'\rangle + \langle\Phi|\uparrow\downarrow\rangle\langle\uparrow\downarrow|\Phi'\rangle$$
$$+ \langle\Phi|\downarrow\uparrow\rangle\langle\downarrow\uparrow|\Phi'\rangle + \langle\Phi|\downarrow\downarrow\rangle\langle\downarrow\downarrow|\Phi'\rangle. \qquad (9)$$

The terms involved in this summation are

$$\langle\uparrow\uparrow|\Phi\rangle = \psi_1^1(\vec{r}_1)\psi_1^2(\vec{r}_2) - \psi_1^2(\vec{r}_1)\psi_1^1(\vec{r}_2),$$
$$\langle\uparrow\downarrow|\Phi\rangle = \psi_1^1(\vec{r}_1)\psi_2^2(\vec{r}_2) - \psi_1^2(\vec{r}_1)\psi_2^1(\vec{r}_2),$$
$$\langle\downarrow\uparrow|\Phi\rangle = \psi_2^1(\vec{r}_1)\psi_1^2(\vec{r}_2) - \psi_2^2(\vec{r}_1)\psi_1^1(\vec{r}_2), \qquad (10)$$
$$\langle\downarrow\downarrow|\Phi\rangle = \psi_2^1(\vec{r}_1)\psi_2^2(\vec{r}_2) - \psi_2^2(\vec{r}_1)\psi_2^1(\vec{r}_2).$$

Writing $\Phi$ explicitly as

$$\Phi(\vec{r}_1,\vec{s}_1,\vec{r}_2,\vec{s}_2)$$
$$= \left[\psi_1^1(\vec{r}_1)e^{i\delta_1}\sin(\alpha_1) + \psi_2^1(\vec{r}_1)\cos(\alpha_1)\right]$$
$$\cdot \left[\psi_1^2(\vec{r}_2)e^{i\delta_2}\sin(\alpha_2) + \psi_2^2(\vec{r}_2)\cos(\alpha_2)\right]$$
$$- \left[\psi_1^2(\vec{r}_1)e^{i\delta_1}\sin(\alpha_1) + \psi_2^2(\vec{r}_1)\cos(\alpha_1)\right]$$
$$\cdot \left[\psi_1^1(\vec{r}_2)e^{i\delta_2}\sin(\alpha_2) + \psi_2^1(\vec{r}_2)\cos(\alpha_2)\right], \qquad (11)$$

it is possible to demonstrate how the summation (10) can be exactly rewritten as an integral over the spin parameters $\alpha_{1,2}$

and $\delta_{1,2}$ in the following way:

$$\langle\Phi|\Phi'\rangle = \mathcal{D}\int\left[\int_0^{2\pi}\Phi(\vec{r}_1,\vec{s}_1,\vec{r}_2,\vec{s}_2)^*\right.$$
$$\left.\times\,\Phi'(\vec{r}_1,\vec{s}_1,\vec{r}_2,\vec{s}_2)d\alpha_1 d\alpha_2 d\delta_1 d\delta_2\right]d\vec{r}_1 d\vec{r}_2, \quad (12)$$

where $\mathcal{D}$ is a constant. In order to prove the above statement, we take into consideration the terms corresponding to $\langle\Phi|\uparrow\uparrow\rangle\langle\uparrow\uparrow|\Phi'\rangle$, since all other terms can be obtained in the same way. First of all we notice that

$$\int_0^{2\pi}d\alpha_i\int_0^{2\pi}d\alpha_j\sin(\alpha_i)\sin(\alpha_j)=\delta_{i,j}2\pi^2,$$
$$\int_0^{2\pi}d\alpha_i\int_0^{2\pi}d\alpha_j\cos(\alpha_i)\cos(\alpha_j)=\delta_{i,j}2\pi^2, \quad (13)$$
$$\int_0^{2\pi}d\alpha_i\int_0^{2\pi}d\alpha_j\sin(\alpha_i)\cos(\alpha_j)=0.$$

This means that only those terms with pairs of sines and cosines of the same angles will give a nonzero contribution. Using these relations we can select only the interesting terms:

$$\int_0^{2\pi}d\alpha_1 d\alpha_2\left[\psi_1^1(\vec{r}_1)^*e^{-i\delta_1}\sin(\alpha_1)\psi_1^2(\vec{r}_2)^*e^{-i\delta_2}\sin(\alpha_2)\right.$$
$$\left.-\,\psi_1^2(\vec{r}_1)^*e^{-i\delta_1}\sin(\alpha_1)\psi_1^1(\vec{r}_2)^*e^{-i\delta_2}\sin(\alpha_2)\right]$$
$$\cdot\left[\psi_1'^1(\vec{r}_1)e^{i\delta_1}\sin(\alpha_1)\psi_1'^2(\vec{r}_2)e^{i\delta_2}\sin(\alpha_2)\right.$$
$$\left.-\,\psi_1'^2(\vec{r}_1)e^{i\delta_1}\sin(\alpha_1)\psi_1'^1(\vec{r}_2)e^{i\delta_2}\sin(\alpha_2)\right], \quad (14)$$

which give

$$\pi^2\left[\psi_1^1(\vec{r}_1)^*\psi_1^2(\vec{r}_2)^*\psi_1'^1(\vec{r}_1)\psi_1'^2(\vec{r}_2)\right.$$
$$+\,\psi_1^2(\vec{r}_1)^*\psi_1^1(\vec{r}_2)^*\psi_1'^2(\vec{r}_1)\psi_1'^1(\vec{r}_2)$$
$$-\,\psi_1^1(\vec{r}_1)^*\psi_1^2(\vec{r}_2)^*\psi_1'^2(\vec{r}_1)\psi_1'^1(\vec{r}_2)$$
$$\left.-\,\psi_1^2(\vec{r}_1)^*\psi_1^1(\vec{r}_2)^*\psi_1'^1(\vec{r}_1)\psi_1'^2(\vec{r}_2)\right], \quad (15)$$

and this is precisely what one would obtain from the products of the first row of Eq. (10). As mentioned above, all the other terms of (10) can be obtained in the same way, proving the equality Eq. (12). Furthermore, one can easily see how the integration over the variables $\delta_i$ is not necessary since these variables appear only as a phase, which exactly cancels out in the nonvanishing terms. Besides this, though the proof of (13) was explicitly given for the particular $N=2$ case, it can be shown that the same relation holds for any $N$. This property holds due to the relations (14), which actually ensure a correct selection of all the necessary terms. The basic idea is that up (down) states of any particle will only be matched to the corresponding up (down) states of the same particle, and this precisely corresponds to projection over a fixed spin state. Since all combinations are taken into account by the presence of both up and down states for all particles, we have accomplished the summation over the entire basis set.

All interesting observables $O$ which can be estimated with VMC, when acting on a Slater determinant, require at most the use of a linear combination of some new Slater determinants. This can be expressed as

$$\langle R,S|O|\Phi\rangle\sum_i\langle R,S|\Phi'_i\rangle, \quad (16)$$

and for linearity the expressions we found can easily be applied. At this point, Eq. (5) can be rewritten as

$$\frac{\int dR d\alpha\,\psi_T^*(R,\alpha)\psi_T(R,\alpha)\frac{O\psi_T(R,\alpha)}{\psi_T(R,\alpha)}}{\int dR d\alpha\,\psi_T^*(R,\alpha)\psi_T(R,\alpha)}, \quad (17)$$

where the spin coordinates of the system $S$ have been rewritten in terms of the parameters set $\alpha$ using (8).

Mapping the sum over the discrete $2^N$-dimensional spin space into an integration over $N$ continuous auxiliary variables allows for a direct VMC integration in an extended space. The overall scaling of the method will not be affected by the presence of additional spin variables, and the computational cost will still show a cubic dependence on $N$. Furthermore, the possibility of treating correlations within a $N^3$ scaling appears very appealing if compared to other costly quantum chemistry methods.

As mentioned earlier, the proposed algorithm does not represent the only possibility for spin summation. A possible alternative could be that of a VMC-sampled sum over the possible spin states, and this would also represent an efficient algorithm.

## III. APPLICATIONS

A broad class of problems exists in which the method discussed above can be applied. Nevertheless, it must also be stressed that it is not always easy to find a good trial wave function when an interaction of the spin-orbit kind is included in the Hamiltonian. This is mainly due to the nonlocality of the spin-orbit interactions.

In order to test the applicability of the method to atomic systems in presence of spin-orbit interactions, we chose to test this method on isolated C, Tl, Pb, Bi, and Po atoms. By investigating both a light atom like carbon and heavier elements, diverse spectra showing very different energy splittings are considered, corresponding to the two distinct limits of $LS$ and $jj$ coupling.[15]

### A. Carbon atom

The carbon atom has six electrons and can be considered as a light element. Although the spin-orbit effects are known to be very small and of little relevance for most properties, they still induce observable splittings in the energy spectrum. Furthermore, the computation of these very small energy differences represents a good starting test for the efficiency of the method. The all-electron Hamiltonian which was employed in the calculations concerning the carbon atom is given by

$$H=\sum_{i=1}\left(\frac{\mathbf{P}_i^2}{2m}+V_{SO}^i-\frac{Z}{\mathbf{r}_i}\right)+\sum_{i<j}\frac{1}{\mathbf{r}_{ij}}, \quad (18)$$

where $V_{SO}^i$ accounts for the spin-orbit interaction for the $ith$ electron. It should be noted that the spin-orbit potential is the only relativistic effect contained in this Hamiltonian. The rest of the relativistic corrections were neglected since they do not contribute to the level splittings if we assume the wave functions given below. The trial wave functions employed in the calculations were linear combinations of Slater determinants of single-particle Hartree-Fock orbitals.[14]

Since the interest, regarding the C atom, was focused on providing a good test for the method using a well-known type of wave function, no optimization was performed, and the combinations of Slater determinants were fixed by the imposed spin-spatial symmetries in the $LS$ coupling.

The spin-orbit interaction in atoms comes from an approximated form of the Dirac equation and can be written (for the $ith$ particle) as

$$V_{SO}^i \psi = -\frac{\hbar^2}{4m^2c^2} i \vec{\sigma}_i \cdot [(\vec{\nabla}_i V) \times \vec{\nabla}_i \psi], \quad (19)$$

where $V$ in this case is the total potential felt by the considered particle. This potential contains both the attractive contribution from the nucleus and the sum of the repulsive interactions with all other electrons. What is commonly done is approximating $V$ with an effective potential $V_{\text{eff}}$ having spherical symmetry. Within this approximation, Eq. (19) can be rewritten as

$$\frac{1}{2m^2c^2} \frac{1}{r} \frac{dV_{\text{eff}}^i}{dr} \vec{L}_i \cdot \vec{S}_i \psi. \quad (20)$$

In case the Coulomb repulsion among electrons is neglected, one is left with a sum of single particle Hamiltonians, and if the factor in Eq. (20) multiplying $\vec{L}_i \cdot \vec{S}_i$ is substituted by a constant, the problem can be exactly solved in analytic form. The term $\vec{L}_i \cdot \vec{S}_i$ in fact commutes with the rest of the Hamiltonian, which is spherically symmetric. However, as soon as the electron-electron Coulomb interaction is taken into account the exact solution is unknown. As already mentioned, since the SO interaction in C is known to yield very small energy splittings, it is reasonable to treat it within the $LS$ coupling procedure. This is done by writing the Hamiltonian (19) as $H = H_1 + H_2$ where $H_2 = \sum_i V_{SO}^i$ and combining eigenstates of $H_1$ (which are eigenstates of both **L** and **S**) in order to obtain eigenstates of **J**. Calling the eigenstates of $H_1$ as $|\gamma L S M_L M_S\rangle$ ($\gamma$ stands for all residual quantum numbers), it may be shown by using the Wigner-Eckart theorem that

$$\langle \gamma L S M_L M_S | H_2 | \gamma L S M_L' M_S' \rangle$$
$$= \mathcal{A} \langle \gamma L S M_L M_S | \mathbf{L} \cdot \mathbf{S} | \gamma L S M_L' M_S' \rangle, \quad (21)$$

where $\mathcal{A}$ is a constant depending on $\gamma L S$. The eigenstates of **J** can be obtained as linear combinations of the $|\gamma L S M_L M_S\rangle$ states and can be denoted as $|\gamma L S J M_J\rangle$. At this point it is easily shown that

$$\langle \gamma L S J M_J | H_2 | \gamma L S J M_J \rangle$$
$$= \frac{1}{2} \mathcal{A} [J(J+1) - L(L+1) - S(S+1)]. \quad (22)$$

Notice how the expectation value of a sum of single-particle terms $H_2$ is related to that of $\mathbf{L} \cdot \mathbf{S}$ (**S** and **L** are the total spin and angular momentum, respectively) by the constant $\mathcal{A}$. This constant contains the effect of the effective potential $V_{\text{eff}}$, and in general it cannot be determined analytically. However, when the SO interaction (20) is approximated by $\mathcal{C}\mathbf{L}_i \cdot \mathbf{S}_i$ with $\mathcal{C}$ constant, $\mathcal{A}$ can be calculated exactly. A first test for our method consisted in verifying the relations above and comparing the numerical result for $\mathcal{A}$ with the analytically computed value. In Table I numerical and analytical results are compared for three different states, showing

TABLE I. Analytical and numerical results for the mean value of the SO interaction ($\mathcal{C} = 1$) and effective coupling constant $\mathcal{A}$ over the three lowest energy states given by fixed $L = 1$, $S = 1$, and $J = 0,1,2$. Results are reported in atomic units.

| L | S | J | Numerical $\langle \sum_i \mathbf{L}_i \cdot \mathbf{S}_i \rangle$ | Analytical $\langle \sum_i \mathbf{L}_i \cdot \mathbf{S}_i \rangle$ | Numerical $\mathcal{A}$ | Analytical $\mathcal{A}$ |
|---|---|---|---|---|---|---|
| 1 | 1 | 0 | −1.001(2) | −1.0 | 0.5005(1) | 0.5 |
| 1 | 1 | 1 | −0.5004(7) | −0.5 | 0.5004(7) | 0.5 |
| 1 | 1 | 2 | 0.4997(5) | 0.5 | 0.4997(5) | 0.5 |

excellent agreement with the predictions of the Wigner-Eckart theorem.

A second set of calculations was then performed, including this time a SO interaction of the form (21) in order to obtain an estimate of the energy splitting induced by the effective spherical potential $V_{\text{eff}}$. The only contributions to the SO splitting in the C atom come from the two occupied $2p$ orbitals; therefore it was only necessary to take the effective potential $V_{\text{eff}}$ for $2p$ electrons into account. Following Slater,[15] in a single-particle picture one could write the effective potential for the particle $i$ as

$$V_{\text{eff}}^i(r) = \frac{Z_{\text{eff}}^i(r)}{r},$$
$$Z_{\text{eff}}^i(r) = Z - \int_0^r \sum_{j \neq i} |\phi_j(\mathbf{r})|^2 d\mathbf{r}. \quad (23)$$

VMC calculations were done for the energy splittings of the lowest energy states ($L = 1$, $S = 1$). The results (see Table II) are in qualitatively good agreement with experimental data.[16] The relative energy differences between ($J = 0, J = 1$) and ($J = 1, J = 2$) states follow the theoretical ratio $1/2$, though they both are too large. The fact that splittings from experimental data do not show the theoretical $1/2$ ratio makes the result for the larger splitting worse. In order to check whether our VMC method would give a correct description also in the case of a realistic SO interaction, further testing was done: in case $V_{\text{eff}}$ is substituted by $Z/r^2$, and the radial parts of the $2p$ single-particle wave functions are given by a single orbital of the Slater type:

$$S_{jl}(r) = N_{jl} r^{n_{jl}-1} \exp(-z_{jl}r),$$
$$N_{jl} = (2z_{jl})^{n_{jl}+1/2} / [(2n_{jl})!]^{1/2}, \quad (24)$$

($n_{ij} = 1,2,3,\dots$ and $z_{ij}$ are fitting parameters), one can obtain an exact analytical form for the SO splitting. Also in this case the numerical results were in excellent agreement with the theoretical predictions.

TABLE II. Numerical results for the mean value of the realistic (20) and effective SO interactions (21) per electron for the three lowest energy states. Results are reported in atomic units.

| L | S | J | Realistic $V_{SO}$ | Effective $V_{SO}$ |
|---|---|---|---|---|
| 1 | 1 | 0 | −2.9(2) ×10⁻⁵ | −3.3(2) ×10⁻⁵ |
| 1 | 1 | 1 | −1.4(1) ×10⁻⁵ | −1.6(1) ×10⁻⁵ |
| 1 | 1 | 2 | 1.4(1) ×10⁻⁵ | 1.7(2) ×10⁻⁵ |

TABLE III. All electrons SO splittings [defined as $E(J) - E(1)$] for C. In the second and third columns VMC predictions relative to the effective SO and realistic SO, respectively. Experimental values in the fourth column. Results are reported in atomic units.

| J | VMC (effective $V_{SO}$) | VMC (realistic $V_{SO}$) | Experimental |
|---|---|---|---|
| 0 | $-10(1.5) \times 10^{-5}$ | $-9(1.5) \times 10^{-5}$ | $-7.5 \times 10^{-5}$ |
| 1 | 0.0 | 0.0 | 0.0 |
| 2 | $20(1) \times 10^{-5}$ | $17(1) \times 10^{-5}$ | $12.3 \times 10^{-5}$ |

In order to check the effects of the approximations contained in the effective spherical potential, calculations were done substituting (21) in the Hamiltonian with the realistic SO interaction (20). Once more, SO potential expectation values were computed for the three lowest energy levels. In this case the energy splittings are reduced with respect to the previous case, becoming closer to experimental data (see Table III). The relative spacings retain the theoretical ratio 1/2 predicted for spherical potentials as before, but the effective SO coupling constant is close to the experimental one, at least for the smaller splitting ($J = 0$, $J = 1$). It remains however about 30% too large in the ($J = 1$, $J = 2$) case.

In the first case the effective screening of the inner electrons appeared to be not effective enough, and one could be led to the conclusion that Hartree-Fock (HF) orbitals do not provide an accurate charge distribution. However, this last calculation showed how, at least for the lowest splitting, the screening effects affecting the SO coupling are reasonably well reproduced in the C atom already at the HF level.

### B. Tl, Pb, Bi, and Po atoms

In order to give a more complete picture of the applicability of the algorithm, the VMC method was also applied to the Tl ($Z = 81$), Pb ($Z = 82$), Bi ($Z = 83$), and Po ($Z = 84$) atoms, which exhibit sizable SO interaction effects. While for C the $LS$ coupling was employed, due to the increased strength of the SO interaction, a better approximation for the description of the energy splittings in heavier atoms is given by the $jj$ coupling scheme. For this reason, the wave function is obtained by combining single-particle $J_i$ (for the $i$th particle) states into the eigenstates of the total angular momentum $J$.

Due to the large number of electrons in the Tl to Po atoms, and the very deep ionic potential, it is customary to limit the explicit degrees of freedom to valence electrons by introducing an effective description in terms of pseudopotentials (or effective core potentials). Although there is no *a priori* limitation in the number of electrons that can be managed in a VMC calculation, very large energy fluctuations coming from the core states are very expensive to average out and are of marginal interest in determining the quantities we are interested in, given that SO splitting is only related to the presence of occupied valence $p$ states. The pseudopotential employed was taken from Kuechle *et al.*,[17] leading to a Hamiltonian (in atomic units) of the following form:

$$-(1/2) \sum_i \nabla_i^2 + V_{pp} + \sum_{i<j} \frac{1}{r_{ij}}, \quad (25)$$

where the indices $i$, $j$ run over the valence electrons, and $V_{pp}$ is the sum of a spin-orbit averaged *ab initio* pseudopotential $V_{av}$, an SO operator $V_{so}$, and a term representing effective charge of the pseudonucleus.

The use of this pseudopotential has the additional benefit of making possible the comparison to the HF results reported in the same reference. In our calculations, the radial parts of $s$ and $p$ orbitals were represented by an expansion in four uncontracted Gaussians. The single-particle orbitals optimization was performed with a variational approach using an adapted implementation of the Fast Inertial Relaxation Engine (FIRE) algorithm.[18] This simple algorithm is based on a molecular dynamics approach to the search in the variational parameters space. The parameter evolution is driven by the forces induced by the total energy partial derivatives, while appropriate cooling is introduced as parameters' motion is stopped whenever the velocities' directions are opposite to the forces. The forces, in turn, are computed during the VMC runs through a sampling of the wave function derivatives with respect to the parameters. Given the form of the trial wave function $\psi_T$, the corresponding differentiation of the energy expectation according to a parameter $\alpha$ is given by

$$\partial_\alpha E_{\psi_T} = \partial_\alpha \frac{\langle \psi_T | H | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle} \quad (26)$$

and can be evaluated following the method also employed by Sorella[13,19] as

$$-2 \frac{\langle \psi_T | H | \psi_T \rangle \langle \psi_T | \partial_\alpha | \psi_T \rangle}{(\langle \psi_T | \psi_T \rangle)^2} + 2 \frac{\langle \psi_T | H \partial_\alpha | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle}. \quad (27)$$

Given the physical relevance of SO splittings in the heavy atoms here considered, the influence of correlation effects was investigated by introducing in the wave function a Jastrow factor[2] of the Pade' form:

$$J(\mathbf{R}) = \exp \left( \sum_{i,j}^{N} V(r_{ij}) \right),$$

$$V(r_{i_{ij}}) = -\frac{r_{ij}}{4(1 + ar_{ij})}, \quad (28)$$

with $a$ being a variational parameter. This factor introduces two-body correlations, which in VMC calculations are usually necessary to obtain a realistic description of the correlation energy. In principle, the Jastrow factor should depend on the relative spin state of the electron pair. In presence of SO interactions inducing a spin rotation, this requirement would lead to a correlated wave function of the form $\prod_{i,j} f_{\sigma\sigma}(r_{ij}) \vec{\sigma}_i \cdot \vec{\sigma}_j$, which would in turn imply the necessity of computing a sum over all the possible two-electron spin states. This sum grows as $2^N$, and becomes very quickly unmanageable. For this reason we prefer, for the moment, to completely neglect the spin dependence in the two-body wave function, focusing on the gross effect of introducing the short range correlations induced by the Coulomb potential. We stress, however, that the introduction of correlation effects already implies a huge improvement with respect to the HF method, keeping the computational cost at a reasonable level.

In computing the SO splittings, the lowest states corresponding to the total angular momentum $J$ eigenvalues, obtained from the multiple occupation of single-particle $p$

TABLE IV. SO splittings for Tl, Pb, Bi, and Po. The second and third columns contain uncorrelated and correlated VMC results, respectively. The fourth and fifth columns report HF results by Kuechle and the relative experimental values.[20] States associated with zero splitting values are taken as a reference. Results are reported in atomic units.

| | J | VMC uncorrelated | VMC+Jastrow | HF | Experimental |
|---|---|---|---|---|---|
| Tl | | | | | |
| | 1/2 | 0.0 | 0.0 | 0.0 | 0.0 |
| | 3/2 | 0.030(5) | 0.031(5) | 0.033 | 0.035 |
| Pb | | | | | |
| | 0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | 1 | 0.032(4) | 0.033(4) | 0.029 | 0.035 |
| | 2 | 0.044(5) | 0.045(5) | 0.046 | 0.048 |
| Bi | | | | | |
| | 3/2 | 0.0 | 0.0 | 0.0 | 0.0 |
| | 3/2 | 0.054(4) | 0.048(6) | 0.057 | 0.052 |
| | 5/2 | 0.074(5) | 0.070(4) | 0.078 | 0.070 |
| Po | | | | | |
| | 2 | 0.0 | 0.0 | 0.0 | 0.0 |
| | 0 | 0.049(8) | 0.043(8) | 0.042 | 0.034 |
| | 1 | 0.080(6) | 0.077(5) | 0.071 | 0.076 |

orbitals, were considered for each atom. Comparing for instance Pb and C, despite the equal number of valence electrons, due to the diverse couplings ($jj$ and $LS$, respectively), these show different splitting patterns. In particular, for Pb the ($J = 0$, $J = 1$) splitting is larger than the difference between ($J = 1$, $J = 2$).

VMC results are reported in Table IV together with the HF results of Kuechle[17] and the corresponding experimental values.[20] Calculations were also performed in absence of correlation by removing the Jastrow factor. Since in this case the trial function is given by the Slater determinant of spinors, we can compare our results with the corresponding HF calculation. A good compatibility is found. Interestingly, correlation effects on the SO splittings appear to be smaller than the statistical error, suggesting that SO effects are mainly determined by the single-particle properties of the wave function. From the comparison among the different data sets we confirm that our VMC calculation shows the correct ordering of the SO splittings among the states considered.

Indeed, our energy differences agree with the other two data sets essentially within the statistical error bars.

## IV. CONCLUSIONS

We introduced an extension of the VMC method capable to realistically describe spin-orbit splittings in heavy atoms. Calculations were tested first in the light C atom, and then extended to a set of heavier open $p$-shell atoms (Ti to Po). We demonstrated that the algorithm provides the correct evaluation of the underlying integrals and, remarkably, leads to sufficient accuracy for resolving the small SO energy differences.

For the case of the carbon atom the small SO splitting is already reasonably well captured within a nonrelativistic Hartree-Fock wave function, although an even more accurate description would require the use of a better variational wave function. Interestingly, the investigation of the effects of the spherical effective SO term showed an appreciable improvement when the more realistic version of the SO coupling operator was employed.

Calculations of SO energy splittings carried on in heavier atoms required a wave functions based on $jj$ rather than $LS$ coupling. In these systems the possibility of a direct optimization of wave functions was investigated. The effects of electron-electron correlations have been studied by introducing in the wave function an explicit, though simplified, two-body Jastrow factor. At this level dynamical quantum correlations seem not to have a huge effect on the SO splittings estimation.

We believe that the obtained results are encouraging, and the method can be applied to more complex systems while retaining the efficiency and robustness of the VMC implementation.

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